

ES&H manual

Environment, Safety, and Health

Volume II

Part 14: Chemical

Document 14.11

Laser Dyes

Recommended for approval by the ES&H Working Group

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New document or new requirements

Approval date: May 30, 2000
Editorial Update: June 25, 2003

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This work performed under the auspices of the U.S. Department of Energy by University of California Lawrence Livermore National Laboratory under Contract W-7405-ENG-48.

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Laser Dyes

1.0 Introduction

Dye lasers normally use a lasing medium that comprises a complex fluorescent organic dye dissolved in an organic solvent. For most laser dyes, little or no toxicology information is available. Several dyes were tested by genetic toxicologists at LLNL using the Ames/*Salmonella* assay (see Appendix A for definition) in the 1980s, and a number were found to be mutagenic. This is often the only toxicological data available for them. The procedures in this document were developed to combine the need for a cautious approach to preventing exposures to hazardous chemicals, proper waste management, fire prevention, and practical operating requirements.

This document contains

- Work practices and precautions for handling laser dyes.
- Procedures for cleaning up laser dyes.
- Waste disposal methods for all laser dyes and laser dye solutions used at LLNL.
- Requirements for personal protective equipment (PPE), facilities and equipment, and fire safety.

These requirements apply to anyone who works with laser dyes and laser-dye solutions, except for laser vendor service representatives, and to all LLNL facilities where operations involving such materials are carried out.

Note: There are no statutory requirements for laser dyes.

2.0 Hazards

Little is known about the toxic properties of laser dyes, except that they are often members of chemical families that contain highly toxic materials. Minor changes in the chemical structure of organic chemicals can have major effects on their toxic properties. Animal experimentation has shown that laser dyes vary greatly in toxicity and potential carcinogenicity. Consequently, laser dyes should be treated as toxic chemicals unless toxicological evidence to the contrary exists. Given the structure of these compounds, a finding that a laser dye is mutagenic suggests that it may be carcinogenic as well. The Ames test is a screening tool for potential carcinogenic activity in mammals, not for the

carcinogenic potency (i.e., the dose needed before the risk of developing a cancer reaches some given level).

The solvent in which the dye is dissolved plays a major role in the hazards. Practically all solvents suitable for dye solutions are flammable and toxic by inhalation and/or skin absorption.

3.0 Controls for Laser Dyes

3.1 Control Classes

LLNL has established three control classes for laser dyes and laser-dye solutions—limited, moderate, and strict. Controls progressively become more stringent as the hazard increases. This follows the philosophy adopted by the National Institutes of Health and the Laser Institute of America in applying controls for biological hazards and lasers, respectively. Controls for the limited- class dyes also apply to moderate- and strict-class dyes, unless modified by controls in those classes. Controls for moderate-class dyes also apply to strict-class dyes, unless modified by controls for strict-class dyes. The control classes are defined as follows:

- **Limited Class.** Laser dyes and laser-dye solutions in this class
 - Are NOT carcinogenic or potentially carcinogenic (based on the Ames/*Salmonella* test), unless contradicted by other biological test data.
 - Lack significant toxicity or, in the absence of comprehensive toxicity data, have a rat or mouse oral LD₅₀ ≥500 mg/kg.
- **Moderate Class.** Laser dyes and laser-dye solutions in this class
 - Are NOT carcinogenic or potentially carcinogenic, or their potential carcinogenicity is unknown.
 - Lack significant toxicity or, in the absence of comprehensive toxicity data, have a rat or mouse oral LD₅₀ <500 mg/kg or an unknown toxicity.
- **Strict Class.** Laser dyes and laser-dye solutions in this class are carcinogenic or potentially carcinogenic. Compounds in this class are treated as carcinogens.

Controls for each class are applied using a graded approach to materials that pose a greater hazard. If the concentration of a moderate- or limited-class dye is below 1% or the concentration of a strict-class dye is below 0.1%, the control class for the solvent determines the control class for the dye solution. When dye concentrations exceed these levels, the control class that applies to the dye shall govern the precautions. See the Laser Dye List for more details.

3.2 Hazard Awareness

Workers shall be familiar with the flammability and known toxicity of all the dyes and solvents that they use; the degree of hazard; and the controls for safely using any dye, solvent, or premixed solution. Workers also shall obtain the material safety data sheet (MSDS) and follow the controls listed for any laser dye powder or dye solution in use. The manufacturer or vendor provides the MSDS for each chemical or product. MSDSs also can be obtained from the LLNL Chemical Inventory Program (ChemTrack), by calling the MSDS hotline (ext. 4-4404), or from the following Internet address:

<http://ctmsds.llnl.gov:1650/livehtml/MSDS/MSDS1.html>

3.2.1 Training

Dye handlers should take HS4242, "Special Training for Toxic Laser Dye Solution." It is an optional half-hour-long class that specifically addresses dye hazards. It can be offered during safety meetings or at other convenient times.

Depending on other chemical handling or chemistry work dye handlers do, it may be necessary for them to take HS4240-CBT, "Chemical Safety," or HS4246-CBT, "Laboratory Safety," depending on whether the person works in a laboratory or nonlaboratory setting. The ES&H Team can provide advice about which classes are needed or to set up HS4242 training. The information needed to determine if either of these courses is needed is found in Document 10.2, "LLNL Health Hazard Communication Program," and Document 14.2, "LLNL Chemical Hygiene Plan for Laboratories," in the *ES&H Manual*.

Those who generate hazardous waste shall take EP0006, "Hazardous Waste Generation and Certification."

3.2.2 Container Labeling

The label shall give the name of the dye and solvent and their percentages, and list the most important hazards associated with the mixture. Solutions containing over 1% of a moderate-control-class dye shall be labeled "Toxic," regardless of the solvent. Solutions containing over 0.1% of a strict-control-class dye shall be labeled "Mutagenic," while weaker solutions of strict-class dyes shall be labeled "Contains mutagen." Labels for

containers of strict-class dyes shall either state that the mixture is mutagenic or, if the concentration is too low to warrant placement in the strict class, that the mixture “Contains mutagen.” Examples of labels are

- “Rhodamine 6G:Ethanol—0.1%:99.9%, flammable, toxic.”
- “DCM:Ethanol—0.05%:99.95%, mutagenic, flammable.”
- “DCM:Ethanol—0.005%:99.995%, flammable, contains mutagen.”
- “Rhodamine 6G:Ethylene glycol—0.2%:99.8%, toxic.”

3.2.3 Posting Laser-Dye Work Areas

Limit access to work areas where dyes are used. Post signs with the name and extension of the Responsible Individual to be contacted at entrances to work areas where laser dyes are in use.

3.3 General Controls for Dyes and Solvents

Limit exposure to laser dyes, solvents, and solutions by minimizing the quantities used and by applying the controls specified in this section.

3.3.1 Solvent Selection

Minimize the use of dioxane, chlorinated hydrocarbons (e.g., ethylene dichloride), and dimethyl sulfoxide (DMSO) solvents; use solvents containing combinations of only carbon, hydrogen, and oxygen whenever practical. Dioxane forms explosive peroxides, especially if the bottle has been opened and allowed to stand for several months or longer. There is equivocal evidence suggesting that dioxane may be a carcinogen. Chlorinated hydrocarbons and DMSO are harder to dispose of than dye solutions containing only carbon, hydrogen, and oxygen. DMSO could increase the toxicity of dyes that contact the skin by expediting the movement of dye through the skin. It also will form corrosive sulfur dioxide when it burns, which would increase the property losses and disruption caused by a fire.

3.3.2 Chemical and Fire Safety

- Keep heat, flames, and other sources of ignition away from solutions of laser dyes in flammable solvents.
- Keep waste solutions containing alcohol, dioxane, or DMSO in approved waste containers. Label these containers as described in Section 3.2.2. Contact the ES&H Team environmental analyst for assistance with determining the appropriate type of container for collecting waste laser-dye solutions.

- Keep oxidizing materials away from dyes and solvents.
- Use and store flammable liquids in accordance with the guidance given in Document 22.5, "Fire," in the *ES&H Manual*.
- Materials used in dye laser systems shall be compatible with the solvents in which the dyes are dissolved and, as far as is known, the dyes.

3.3.3 Hazardous Waste

Waste dyes, dye solutions, disposable protective clothing, and materials and equipment contaminated with dye residues are hazardous waste. Contact the Hazardous Waste Management (HWM) technician for assistance with packaging, labeling, and removing laser-dye waste from the workplace. Contact the ES&H Team environmental analyst for assistance in determining the appropriate type of container for collecting waste laser-dye solutions.

3.3.4 Taking Dye-Laser Systems Out of Service

Dye systems or components being taken out of service, whether they are being disposed of or if the room is being vacated with the equipment left in place, shall be labeled to show what dyes were last handled in the systems or components. The label should be attached to the dye pump or to the component, as applicable.

3.3.5 Procurement of Premixed Dye Solutions

The MSDS shall be obtained for dye solutions premixed by the manufacturer.

3.3.6 Dyes for Nonresearch Uses

Dyes developed by LLNL shall receive toxicological evaluation and testing if they are to be sold commercially or made available for commercial or military use. Arrangements for testing shall be made with the knowledge and agreement of the area ES&H Team industrial hygienist and the Technical Support and Policy Development Division of Hazards Control.

3.3.7 Integration Work Sheets and Documentation

An IWS shall be prepared for work involving laser dyes. A generic IWS or folding laser dye issues into an IWS prepared for other reasons shall suffice, provided the full range of hazards encountered during dye work is reviewed. Safety Plans (SP) are not required unless controls depart from those given in this document.

3.4 Controls for Limited-Class Dyes

The general controls in Section 3.3 and those below apply to *all* classes of laser dyes, unless amended by subsequent sections to this document.

3.4.1 Work Practices

- Do not eat; drink; smoke; or store food, beverages, or smoking materials in work areas where laser dyes are in use.
- Post caution signs conspicuously at entrances to and in work areas where laser dyes are in use.
- Use mechanical pipetting aids when handling dye solutions.
- Keep containers of solvents and dye solutions closed.
- Cap off and/or drain dye lines that are not in use.
- Label containers and dye plumbing clearly with the name of the dye or solvent and the concentration of the solution. Mark “TOXIC” on the container if ethylene glycol is used as the solvent or “FLAMMABLE” if an alcohol is used.
- Keep the work area where dyes are used clean. Clean up after experiments; precautions described in the sections about spill cleanup can be used as a guide for developing cleanup procedures. Remove visible stains as much as practical during cleanup.

Note: Janitors shall not do dye cleanup work.

- Store containers in a cool place. Keep flammable solvents in approved flammable-liquid safety containers.
- Store, handle, and use dioxane and other peroxidizable compounds in accordance with Document 14.1, “Chemicals,” in the *ES&H Manual*. See *Standard for Storing and Using Peroxidizable Organic Chemicals*, UCRL-AR-133218 for a listing of peroxidizable compounds.
- Transport solutions in containers made of impact-resistant, compatible material. Make sure these containers are sealed and labeled as described in Section 3.2.2.
- Wash hands after handling laser dyes and solutions.

3.4.2 Personal Protective Equipment

- Use safety eyewear as specified in Document 11.1, “Personal Protection Equipment,” in the *ES&H Manual*.

- Use impervious gloves when handling dye powders. Table 1 provides general information about gloves that are compatible with various dye solvents. If the glove/solvent combination is marked “OK”, it is probably compatible. However, this compatibility should be confirmed with vendor data. If a glove/solvent combination is not marked “OK”, it is not compatible or there is no data available.

Table 1. Protective glove recommendations for laser dye solvents.

Solvents	Glove type ^a							
	Neoprene	Butyl	PVC	Nitrile	Disposable latex ^b	Natural rubber	Viton®	4H ^c
Benzyl alcohol	OK	OK	—	—	—	—	OK	—
Dimethyl sulfoxide (DMSO)	—	OK	—	—	—	—	—	—
Ethanol (ethyl alcohol)	—	OK	—	—	—	—	—	OK
Ethylene glycol	OK	OK	OK	OK	—	OK	OK	OK
Ethylene glycol phenyl ether (2-phenoxyethanol)	—	OK	—	OK	—	—	—	—
Glycerol (glycerin)	OK	OK	OK	OK	—	OK	OK	OK
Methanol (methyl alcohol)	OK	OK	OK	OK	—	OK	—	OK
Propylene carbonate	—	OK	—	OK	—	—	—	—

a Check vendor data. Do not use these glove/solvent combinations even if marked “OK” if the vendor’s data are not available.

b Disposable latex gloves can be used, except for dyes in the strict classification, provided they are inspected before use for tears, cracks, holes, weak spots, embrittlement, discoloration, and other signs of damage and are never reused.

c A trademark of Safety 4.

d Viton® is a registered trademark of DuPont Elastomers.

3.4.3 Facilities and Equipment

- Ensure that an eyewash and/or shower is located within a walking distance of 100 ft or a walking time of 10 sec. from dye and solvent plumbing systems and handling areas. Shorter distances may be warranted depending on the hazards of the operation and the layout of the work area (e.g., doors and potential obstacles in the path).
- Install spill pans under pumps and reservoirs or, preferably, enclose them. Make sure that knobs and other protuberances extend through the holes in the enclosures.

3.4.4 Spill Cleanup

- Call 911 for help if people are injured or if help is needed from the Fire Department.
- Use gloves, safety eyewear, and respirators to protect against dust and solvent exposures when cleaning up spills.
- Clean up small spills (≤ 500 ml) with absorbent material (e.g., Kimwipes or “kitty litter”). If the spill is > 500 ml, call the area health and safety technician for assistance.

3.5 Controls for Moderate-Class Dyes

The general and limited-class controls in Sections 3.3 and 3.4 and those below apply to the moderate class of laser dyes.

3.5.1 Work Practices

- Mix dyes in a laboratory fume hood or glove box that provides a designed face/opening velocity of 100 ft/min. Do not use a hood that blows back inside a building, even if the exhaust is filtered.
- Call the area health and safety technician for assistance if exposure to dye powder is possible.
- Keep waste solutions containing alcohol, dioxane, or DMSO in approved waste containers. Contact the ES&H Team environmental analyst for assistance with determining the appropriate type of container for collecting waste laser-dye solutions.

3.5.2 Personal Protective Equipment

Use a disposable laboratory coat or disposable coveralls when handling or mixing dyes and when cleaning up spills.

3.5.3 Facilities and Equipment

Apply the controls in Section 3.4.3.

3.5.4 Spill Cleanup

Apply the controls in Section 3.4.4.

3.6 Controls for Strict-Class Dyes

All the general, limited, and moderate controls in Sections 3.3–3.5 as well as those listed below apply to dyes in the strict class.

3.6.1 Work Practices

- Minimize the quantity of pure dye or solutions containing >0.1% of dye in storage or in use at any time.



Mutagenic dye work area.

Authorized personnel only.

Contact:

Extension: _____

- Limit access to work areas where dyes are used. Post signs, such as that above, with the name and extension of the Responsible Individual to be contacted at entrances to work areas where strict-control-class laser dyes are in use.
- Make sure maintenance and emergency personnel know of problems they can encounter in strict-control-class dye work areas prior to entering.
- Use vacuum cleaners approved for toxic dust service or wet methods for housekeeping in dye work areas.
- Make sure the mixing-hood exhaust does not recirculate into the work area and passes through a high-efficiency particulate air (HEPA) filter.
- Store dye powders or dye solutions containing >0.1% of dye in closed containers that are, in turn, kept in closed outer containers. Label both containers clearly with the name of the dye or solvent and its concentration. Mark “TOXIC—MUTAGENIC” or “FLAMMABLE” on the container if alcohol, dioxane, or DMSO is used as a solvent.
- Transport laser dyes and laser-dye solutions in double containers. Make sure that the inner containers used to transport these substances are made of impact-resistant and chemically compatible material and that the outer containers are made of impact-resistant materials. Insert compatible

absorbent material in the space between the inner and outer containers, and seal and label both containers.

- Keep all waste solutions classified as “strict” in approved waste containers labeled “TOXIC—MUTAGENIC” or “FLAMMABLE,” as appropriate.
- Leak-test dye-pump loops, as appropriate.

3.6.2 Personal Protective Equipment

Apply the controls in Section 3.4.2. In addition, use disposable clothing (either a disposable coverall or disposable laboratory coat). Dispose of used clothing in accordance with directions of the building hazardous waste technician.

3.6.3 Facilities and Equipment

- To make cleaning easy, use benches, floors, and storage spaces with as few cracks, crevices, hard-to-reach places, and matte-textured surfaces as possible. Avoid using dark-colored materials that hide stains and installing dye-handling equipment on false floors.
- Make sure that articles contaminated with dyes are stored separately from those that are not.
- Store pure dyes, dye solutions, and wastes containing $\geq 0.1\%$ of a dye in a designated storage space in the dye work area.
- Enclose dye pumps and reservoirs. Make sure that knobs and other protuberances extend through the holes in the enclosures.
- Design equipment to minimize leakage.
- Provide a laboratory fume hood or totally enclosing hood (glove box) for mixing dyes. Aerodynamically contoured balance enclosures are available. The face velocity for a laboratory hood or the air velocity through any opening of an enclosing hood shall be 100 ft/min when used for dye mixing. The hood exhaust must pass through a HEPA filter. Do not use a hood that exhausts back inside a building.

3.6.4 Spill Cleanup

- When cleaning up spills, use gloves, protective eyewear, and respirators in accordance with Document 11.1. Filtering facepieces shall not be used. Contact your ES&H Team industrial hygienist for guidance in selecting respirators.

- Keep people out of the area where a spill has occurred. Call the health and safety technician for assistance if exposure to dye powders or dye concentrations above 0.1% is possible. Report small spills and cleanups to the area health and safety technician.
- Do a final cleanup check for spills of DCM and other mutagenic dyes using the Ames assay DMSO swipe technique.

3.7 Waste Disposal

- Dispose of used dye powders or dye solutions absorbed into solids and dye-soiled objects (including PPE) in sealed, polyethylene (not PVC) plastic bags. Use the following label or one which conveys the same information which can be hand written or printed when the waste contains solvent-soaked materials.



Solvent-soaked materials may be highly flammable.

Immediately place the sealed bags inside sealed drums, then attach a properly completed Hazardous Waste Label and a black-and-white Hazardous Waste Continuation Label to the drums in accordance with the requirements in Document 36.3, "Management of Satellite and Waste Accumulation Areas," in the *ES&H Manual*.

- Do not package DMSO wastes with other wastes. Place DMSO wastes in separate containers for disposal by Hazardous Waste Management.
- Dispose of dye solutions in designated drums located in Satellite Accumulation (workplace) Areas. Keep a waste log of the dyes and solvents, the amounts of each emptied into the drum, and the name of the individual who disposed of the waste. Put this information on the Hazardous Waste Continuation Label each time waste is emptied into the drum.
- When disposing of rinsewater or wastewater that is potentially contaminated with dye or dye solutions, use drains that are connected to retention tanks or carboys and approved for laser-dye service. Avoid discharging other chemical wastes or domestic wastewater into laser-dye retention tanks.

4.0 Responsibilities

General responsibilities for all workers are described in Document 2.1, “Laboratory & ES&H Policies, General Worker Responsibilities, and Integrated Safety Management,” in the *ES&H Manual*. Specific responsibilities regarding laser dyes and laser-dye solutions are listed under each title.

4.1 Workers

- Be familiar with the toxicity and flammability of all dyes and solvents; the degree of hazard; and the controls for safely using all dyes, solvents, and solutions.
- Follow the provisions of this document and apply the controls specified here and, when applicable, IWSs or SPs for any laser-dye powder or dye solution in use. Contact your work supervisor for guidance when in doubt about any aspect of dye or solvent handling.

4.2 Work Supervisors

- Ensure that workers follow the procedures in this document and promptly respond to spills involving dyes.
- Contact your area ES&H Team if you have questions (e.g., assigning a control class) about handling laser dyes.

4.3 ES&H Teams

- Give workers advice about the controls and protective equipment necessary for work involving laser dyes and dye solvents.
- Assist with spills and incidents involving laser dyes.
- Provide dye safety training upon request.
- Provide guidance for the management of laser-dye waste.

4.4 Safety Programs Division

The Hazards Control Safety Programs Division maintains a list of dyes and solvents in use and assigns each to the appropriate control class.

4.5 Health Services Department

Health Services will review exposure and toxicology information related to laser dyes and may implement medical surveillance and biological monitoring programs for workers who handle the strict class of dyes. Workers involved in accidental exposures also may be included in surveillance programs.

5.0 Work Standards

29 CFR 1910, Subpart Z, "Toxic & Hazardous Substances."

40 CFR 262, "Standards Applicable to Generators of Hazardous Waste."

49 CFR 100-199, "Research and Special Programs Administration."

ACGIH TLVs and BEIs: Threshold Limit Values for Chemical Substances and Physical Agents, 2002 (excluding Biological Exposure Indices, TLVs for Physical Agents, and Biologically Derived Airborne Contaminants).

ANSI Z9.5-1992, "American National Standard for Laboratory Ventilation," Sections 5.7 and 5.8.

ANSI Z358.1-1990, "American National Standard for Emergency Eyewash and Shower Equipment." (Testing frequency for emergency showers should be monthly rather than weekly as required by the standards.)

NFPA 45, "Standard on Fire Protection for Laboratories using Chemicals," 1996 edition.

UCRL-AR-133354, Rev 2 (April 2003), *HEPA Filter and In-place Leak Testing Standard*."

UCRL-AR-129189, *Occupational Medicine Standard for Medical Evaluation of Employees*.

6.0 Resources for More Information

6.1 LLNL Contacts

Contact the area ES&H Team for guidance on classifying laser dyes and laser-dye solutions, training, workplace evaluations, and waste-disposal procedures.

6.2 Lessons Learned

Refer to the following Internet address for lessons learned applicable laser dyes and dye solutions:

http://www-r.llnl.gov/es_and_h/lessons/lessons.shtml

Appendix A

Terms and Definitions

Ames assay	A screening biological test for genetic toxicity using <i>Salmonella typhimurium</i> bacteria. This test is a predictor of mutagenicity in mammals for chemicals with structures similar to those used in laser dyes.
Carcinogenic	Capable of causing cancer in mammals.
Chlorinated hydrocarbons	Compounds containing carbon, hydrogen, and chlorine often used as solvents.
DCM	4-Dicyanomethylene-2-methyl-6-p-diethylaminostyryl-4-H-pyran, a laser dye.
Dioxane	A solvent from the “ether” family. Ethers form explosive “peroxide” compounds on prolonged contact with air. See Document 14.1 for further information about the properties and precautions for peroxide-forming compounds.
DMSO	Dimethyl sulfoxide. A solvent that has the unusual property of expediting the passage of materials through intact skin.
Ethylene dichloride	A chlorinated hydrocarbon that has consistently behaved as though it could be a carcinogen in various biological tests.
HEPA	High-efficiency particulate air [filter].
LD ₅₀	Lethal dose for 50% of animals tested, usually given as mass of chemical per animal body mass in mg/kg.
MSDS	Material safety data sheet.
Mutagenic	Capable of causing changes in the genetic makeup of an organism.
PVC	Polyvinyl chloride.
<i>Salmonella</i>	A genus of bacteria used in the Ames assay.
Toxicology	The study of poisons and the adverse effects of substances and agents on living organisms.